Binary Critical Fluid Mixtures for Extraction, Fractionation, and Reaction Chemistry

J.W. King
NCAUR-ARS/USDA
1815 N. University St.
Peoria, IL 61604 U.S.A.

K. Lee and A.A. Clifford
University of Leeds
School of Chemistry
Leeds LS2 9JT, United Kingdom

Binary mixtures of such fluids as carbon dioxide, hydrogen, helium, nitrogen, and tetrafluoroethane find considerable utility as selective extraction and reaction media. In this presentation, the relevant critical properties and phase equilibria for such mixtures will be cited to define the critical loci and, hence, the one- and two-phase regions. Depending on the relevant critical temperatures or pressures, one fluid can enhance the solubility of a solute in the mixture or conversely act as an anti-solvent with respect to the solute. Computed phase diagrams are capable of verifying operation in the one-phase region, or the occurrence of the two-phase region, which may or may not be deleterious for extraction or reaction purposes. Whereas consideration of the cohesive energy densities of the single fluids provides an empirical basis for their exhibited miscibility (e.g., gas-gas miscibility); such an approach cannot account for the degree of solubility enhancement or loss exhibited by solutes in such mixtures

Several examples will be provided for using the above binary fluid mixtures both in process and analytical chemistry. Discrete mixtures of carbon dioxide in the supercritical state with helium or nitrogen have proven to be a selective extraction medium for trace analyte isolation in the presence of lipid coextractives. Experimental verification of this observation has been achieved with an apparatus capable of measuring simultaneously solute solubilities, fluid extraction density, and composition; while altering the composition, temperature, and pressure of the fluid mixture. Similarly, this apparatus has been used to conduct hydrogenation of oleochemicals in supercritical carbon dioxide and hydrogen or propane mixtures at elevated temperatures, producing products of desired physical properties for industrial use. The unique extraction properties of fluoroform or tetrafluoroethane with supercritical carbon dioxide will also be cited for enhancing the solubility of pesticides from different sample matrices.